Industrial and Analytical Instruments and Services

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- Investigation of Arsenic Oxidation State Speciation in Primary Calibration Solutions and Effects on ICP-OES Measurements

Program: Industrial and Analytical Instruments and Services

Title: Critical Reference Materials for Mineral Commodities

Authors: J.R. Sieber, A.F. Marlow, S.A. Wilson (USGS), and J.T. Wolsiefer, Sr. (Silica Fume Assoc.)

Abstract: The Analytical Chemistry Division has long supported United States industries that rely on mineral resources. SRM 1d Argillaceous Limestone exemplifies this long-term commitment. Versions of SRM 1 have been provided by NBS/NIST since 1910. In contrast, new SRM 2696 Silica Fume exemplifies our responsiveness to new technology. SRM 2696 was developed to support manufacture and use of this high-grade, small particle size silica used to improve the strength and durability of concrete. Silica fume, a by-product of metals refining, metamorphosed from industrial waste to an important commodity in the past five to ten years.

Impact: Mineral wealth has always been a key element of a successful economy. As technology evolves, new mineral resources are exploited. However, older industries like construction and transportation still extract huge quantities of minerals. Over the years, the quality demands of these older industries have become more stringent, and their laboratories continue to find better ways to analyze raw materials and by-products. Consequently, they still need SRMs for the minerals they've been using for many years, but now, they need higher quality information. Plus, they need SRMs for byproducts, which are transformed into useful products ever more frequently as sustainability becomes a key element of economic planning.

SRM 1d is the fourth version of this important material. Argillaceous limestone – meaning 'containing clay' – is a critical natural resource. Besides its use as a building material, it is used to manufacture lime for agricultural and chemical processes, cement and concrete, and iron and steel. ASTM International Committee E01 on Analytical Chemistry of Metals, Ores, and Related Materials, Committee C01 on Cement, Committee C07 on Lime and Limestone, Committee C09 on Concrete and Concrete Aggregates, and the National Lime Association expressed support for renewal of SRM 1c. Like its predecessors, SRM 1d will be used extensively for validation of ASTM International and in-house test methods at hundreds of laboratories around the world.

Standard Reference Material 2696 Silica Fume is the culmination of collaboration by the Silica Fume Association and NIST with support from the Federal Highway Administration. SRM 2696 is intended primarily for evaluating chemical and instrumental methods of analysis of silica fume to satisfy product specifications. Certified values were established for silicon (as SiO_2) and six other chemical constituents, plus reference values for five constituents and Specific Surface Area by nitrogen absorption. All values are products of extensive testing by NIST and collaborating laboratories from manufacturers, distributors, state transportation departments, universities, and commercial laboratories. This allows us to leverage their expertise without the investment needed to develop it ourselves.

High-Performance Concrete containing silica fume can have very high compressive strength and durability due to low permeability. Reduced permeability helps prevent spalling due to the corrosion of steel reinforcing bars inside the structure following the infiltration of chlorine from

salt. Silica fume is a byproduct of producing silicon metal and ferrosilicon alloys. No longer discarded in landfills, more and more silica fume is being used in concrete instead. Increasingly, state highway and transportation administrations require high-performance concrete in bridges and roadways. In response to the demand and to protect against the use of contaminated material, standard-writing organizations around the world are implementing specifications for the chemical composition and physical properties of silica fume.

Accomplishments: Both SRM 1d and SRM 2696 were certified using X-ray fluorescence spectrometry (XRF) with borate fusion sample preparation in the matrix-independent approach developed during an Exploratory Research project several years ago [1,2]. Certified values were assigned after combining NIST XRF results with results from the private laboratories.

SRM 1d is certified for 12 constituents, with four reference values and 28 information values. In contrast, SRM 1c was certified for 11 chemical constituents. Table 1 provides a side-by-side comparison of SRM 1c and SRM 1d to illustrate the improvements in analytical uncertainty over a span of 25 years.

Future Plans: In the coming year, the level of activity in support of mineral commodities will remain at about the same level. Ongoing projects include the renewal of SRM 331 Copper Ore Mill Tails in support of the copper mining and refining industry and the renewal of SRM 57a, Silicon Metal in support of silicon refiners and their customers. In addition, plans are in place to begin renewals of three high-demand soil SRMs – SRMs 2709, 2710, and 2711.

References:

1. Sieber, J. R., *Matrix-Independent XRF Methods for Certification of Standard Reference Materials*; Adv. X-Ray Anal., <u>45</u>, 2002.

2. Sieber, J.; Broton, D.; Fales, C.; Leigh, S.; MacDonald, B.; Marlow, A.; Nettles, S.; and Yen, J.; *Standard Reference Materials for Cements*; Cem. Concr. Res., <u>32</u>, 1899-1906 (2002).

Table 1. Comparison of Values and Uncertainty Estimates[a] for Limestone SRMs.

Constituent	SRM 1c		SRM 1d	
	December 1978		October 2004	
SiO_2	6.84 ± 0.16	$(2.3\ \%)$[b]	4.080 ± 0.071	$(1.7\ \%)$[b]
Fe_2O_3	0.55 ± 0.06	$(11\ \%)$	0.3191 ± 0.0068	$(2.1\ \%)$
Al_2O_3	1.30 ± 0.06	$(4.6\ \%)$	0.526 ± 0.013	$(2.5\ \%)$
TiO_2[c]	0.07 ± 0.02	$(29\ \%)$	0.0306 ± 0.0065	$(2.1\ \%)$
P_2O_5	0.04 ± 0.02	$(50\ \%)$	0.0413 ± 0.0025	$(6.1\ \%)$
MnO[d]	0.025 ± 0.01	$(40\ \%)$	0.0105 ± 0.0003	$(2.9\ \%)$
CaO	$50.3\ \pm\ 0.6$	$(1.2\ \%)$	$52.85\ \pm\ 0.16$	$(0.3\ \%)$
SrO	0.030 ± 0.01	$(33\ \%)$	0.0303 ± 0.0010	$(3.3\ \%)$
MgO	0.42 ± 0.08	$(19\ \%)$	0.301 ± 0.010	$(3.3\ \%)$
Na_2O	0.02 ± 0.02	$(100\ \%)$	0.0109 ± 0.0016	$(1.5\ \%)$
K_2O	0.28 ± 0.02	$(7.1\ \%)$	0.1358 ± 0.0046	$(3.4\ \%)$
S	Not determined		0.1028 ± 0.0062	$(6.0\ \%)$
ZnO	Not determined		0.0022 ± 0.0003	$(14\ \%)$

[a] Due to changes in definitions since 1978, the uncertainties for SRM 1c were multiplied by an expansion factor of 2 to make them comparable with SRM 1d.
[b] The relative uncertainty is given in parentheses.
[c] This constituent is a reference value for SRM 1d.
[d] Mn is certified as the element in SRM 1d.

Program: Industrial and Analytical Instruments and Services

Title: Characterization of the New Thermal Neutron Prompt Gamma Ray Activation Analysis Instrument

Authors: E.A. Mackey, D.L. Anderson[1], P.J. Liposky[2], R.M. Lindstrom, H. Chen Mayer, and G.P. Lamaze

[1]US Food and Drug Administration, Elemental Research Branch, College Park, MD 20740-3835
[2]NIST, Center for Neutron Research, Gaithersburg MD, 20899-8561

> PGAA limits of detection have been greatly reduced compared with those of the original instrument due to reduced gamma-ray backgrounds and increased element sensitivities.

Abstract: A new thermal neutron PGAA instrument was built at the NIST Center for Neutron Research. It replaced the original PGAA instrument that was built in the late 1970's. This new instrument provides greater sensitivities, better detection limits, and much lower background radiation. The new instrument is also easier and safer to assemble for use.

Purpose: The new thermal neutron prompt γ-ray activation analysis instrument was designed to provide greater sensitivities, better detection limits, and much lower background radiation. (See Figure 1.) Experiments were performed to measure the improvements in element sensitivities and background count rates.

Major Accomplishments: A sapphire filter was placed in the neutron beam shutter assembly to reduce the fast neutron and low energy γ-ray components of the beam. The fast neutron component of the beam was reduced by a factor of five and the low energy background γ-radiation by factors of 5 to 10. A new external beam tube, sample chamber, beam stop, and support structure were built and a new detection system installed. The new beam tube is made of two cylindrical aluminum sections lined with a lithiated polymer. The sample chamber was also fabricated from aluminum and lined with lithiated polymer, and may be evacuated to minimize the number of neutrons scattered and absorbed by air. The beam tube and sample chamber assembly is suspended from the aluminum support structure. The detection system consists of a 40% efficient germanium detector (resolution 2.0 keV at 1332.5 keV) and bismuth germanate Compton suppressor. The detection system shield consists of lead surrounded by borated and lithiated polyethylene, placed on a table attached to the support structure. The new, more compact beam stop is welded to the support structure. Capture gamma-ray photopeaks from H, B, C, N, Na, Al, Fe, Ge, I, and Pb in the background spectrum were either of lower intensity or eliminated with the new PGAA instrument. The improved detection system, positioned closer to the sample, increased element sensitivity by 5% to 50%. During the past year work was completed on the determination of 0.1% N in oil materials which would not have been possible without the previous instrument. We have also completed a complete uncertainty assessment for this method and this instrument.

Impact: The new PGAA instrument is safer to assemble for use and provides greater sensitivities, better detection limits, and much lower background radiation. Analyses of SRMs and other materials will benefit from these improvements.

Future Plans: Additional work is in progress to prepare a suite of standards for the elements of interest for a broad range of neutron absorption and scattering matrices.

Program: Industrial And Analytical Instruments and Services

Title: New Series of Standard Reference Materials (SRMs) for Raman Intensity Correction

**Authors:**   S. J. Choquette, W. Hurst, and E. Etz

Purpose: Raman spectroscopy is a nondestructive analytical method that has many qualitative and quantitative analytical applications in the homeland security, forensic, pharmaceutical and biotechnology industries. It's major advantage over IR spectroscopy as an analytical tool is that it may be used with little or no sample preparation. Because Raman scattering is a single beam emission process, the appearance of a compound's Raman spectra is highly dependent on the wavelength of the excitation source and the construction of the spectrometer. As a result, Raman spectral libraries are only useful for the specific instrument configuration upon which the spectra were measured. The development of a simple to use emission standard would allow the user to correct the sample spectra for instrument response. Corrected spectra, much like absorbance spectra, would be transferable between instruments, would be amenable to searching in corrected libraries, and would allow verification of instrument performance.

Context: This work is part of a collaborative effort between division 839, 836 and 837 to develop a suite of inexpensive intensity correction standards for commercial Raman systems employing a number of laser excitation wavelengths. Currently three standards have been produced that are suitable for use with systems employing 785 nm lasers (SRM 2241), 532 nm lasers (SRM 2242) and 488/514.5nm lasers (SRM 2243). The development of the standards will allow a traceable calibration of the system response to NIST standards, which is a necessary step for qualification of chemical instrumentation in the pharmaceutical industry. In addition, the use of these standards will enable the creation of standardized Raman spectral libraries, an increasingly important task given the number of spectrometer vendors marketing this technique to 1st responders, forensic scientists and military personnel.

Major Accomplishments: This year we completed work on SRM 2243: a relative intensity correction standard for 488/514.5 nm systems and initiated work on SRM 2244: a relative intensity correction standard for 1064 nm lasers. The later is particularly important as our customer base for SRM 2244 is the pharmaceutical industry. FT Raman systems are widely used in this industry because of the large installed base of FT-IR systems (similar instruments/software) and also the Raman spectra of compounds excited with NIR excitation tend to exhibit less fluorescence interference. We have identified a suitable candidate glass for SRM 2244 and have initiated a round robin study with a number of instrument vendors to assess compatibility and utility of the glass. Based upon favorable feedback concerning this glass, a production melt was procured and is currently being processed by our glass shops. We anticipate delivery of this SRM in FY 2005.

The following graph depicts the uncorrected Raman spectrum of cyclohexane acquired on three different Raman systems. All three spectrometers used 785 nm laser excitation. As can be seen, the height of the bands is different with each spectrometer. The next graph shows that same spectra corrected with SRM 2241. The band heights of the spectrum are now similar.

Cyclohexane Raman Spectra on three Raman spectrometers utilizing 785 nm excitation.
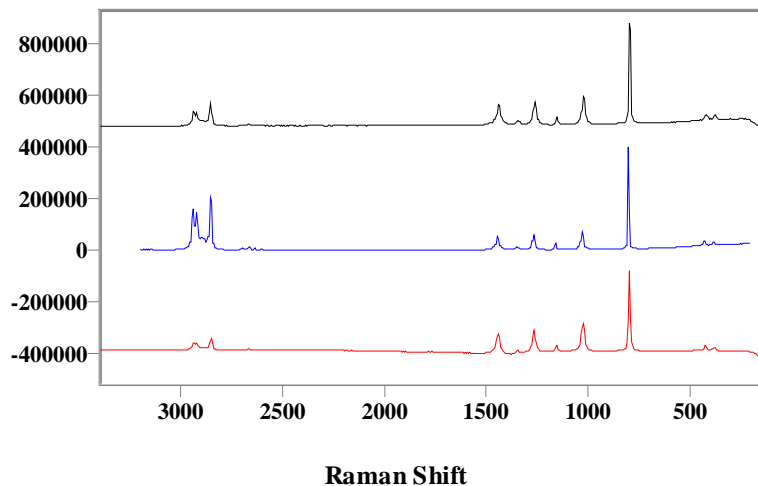
SRM 2241 corrected Raman spectra of cyclohexane on the same spectrometers.
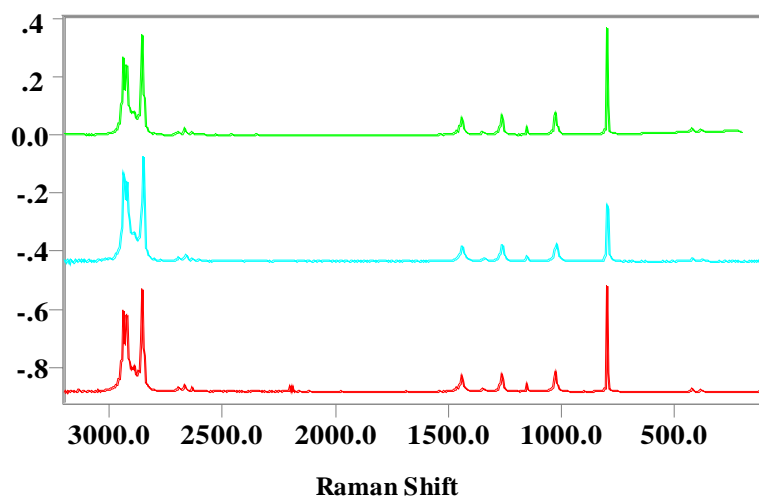
Program: Industrial and Analytical Instruments and Services

Title: Fluorescence Standards Suite for Spectral Correction of Fluorometers

Authors: P.C. DeRose, D.H. Blackburn, and G.W. Kramer

Vision: To prepare, characterize and certify a set of fluorescent glass SRMs that will enable the shape and intensity of spectral emission to be calibrated on fluorometers in the near UV and visible regions of the spectrum.

Purpose: Luminescence measurements have become the detection methods of choice for new clinical and biochemical assays, and related high-throughput techniques, due to their extraordinary selectivity and sensitivity. These new analytical methods are becoming increasingly more quantitative, requiring standards to calibrate the luminescence measuring instruments that they utilize and aid in the validation of the methods. Ideally, users would like to employ the same organic dye probes used for analyte detection as standards for fluorescence intensity and spectral correction. Unfortunately, organic dyes photobleach quickly, do not have long shelf lives in solution, have environment dependent fluorescence and are expensive to produce at high purity.

Scientific Research: After studying the characteristics of the different types of fluorescent materials, we found metal oxide doped (MOD) glasses to be the best choice for use as fluorescence standards for spectral correction and intensity. These glasses are photostable, robust, relatively inexpensive and can be made to suit most detection formats. Our research-grade fluorometer is being used to characterize the spectral characteristics of a series of MOD glasses to determine which will have the correct spectral shape and intensity for appropriate standards. A UV light chamber and a laser are also being used to irradiate the candidate glasses over a timed period. The fluorescence intensity of each glass is measured before and after irradiation to determine its rate of photodegradation.

Major Accomplishments: Spectral emissivity standard candidates have been identified with UV/violet, blue, green and yellow/orange fluorescence, corresponding to CeO_2, CuO, U_3O_8 and MnO_2 dopants, respectively. At this point, the U_3O_8 and MnO_2 glasses have been most thoroughly studied. They are both highly resistant to photodegradation and possess all of the desired characteristics for spectral emissivity standards. They are presently in the final stage of production and are expected to be certified within the next year. These standards are being made in the form of a standard sized cuvette with three polished long faces for 90-degree detection and one frosted long face for front-face detection. The CeO_2 and CuO glasses have both been shown to have desirable spectral characteristics and are presently in the prototype stage of development.

Context and Impact: Once certified, the U_3O_8 and MnO_2 glasses can be used in combination with SRM 936a quinine sulfate dihydrate; a blue spectral emissivity standard that is the only standard presently sold for spectral correction of fluorometers; to cover the visible region from 400 nm to 700 nm (see Figure). The CeO_2 glass will be used to cover the near UV/violet from 350 nm to 450 nm. We hope to replace SRM 936a with the CuO glass, as the present standard is an organic dye that has many of the stability problems associated with organic fluorophores.

Since all of these glasses are highly resistant to photodegradation, they can also be used as day-to-day intensity standards for instrument qualification.

Future Plans: We have not yet found a suitable MOD glass for a red emission standard that would cover the region from approximately 680 nm to 800 nm, and beyond. We are presently working with a nanocrystal manufacturer to help us to identify such a nanocrystal-based material. We are also working with the same manufacturer and a glass manufacturer to develop fluorescent thin films to be used as intensity standards for microarray readers.
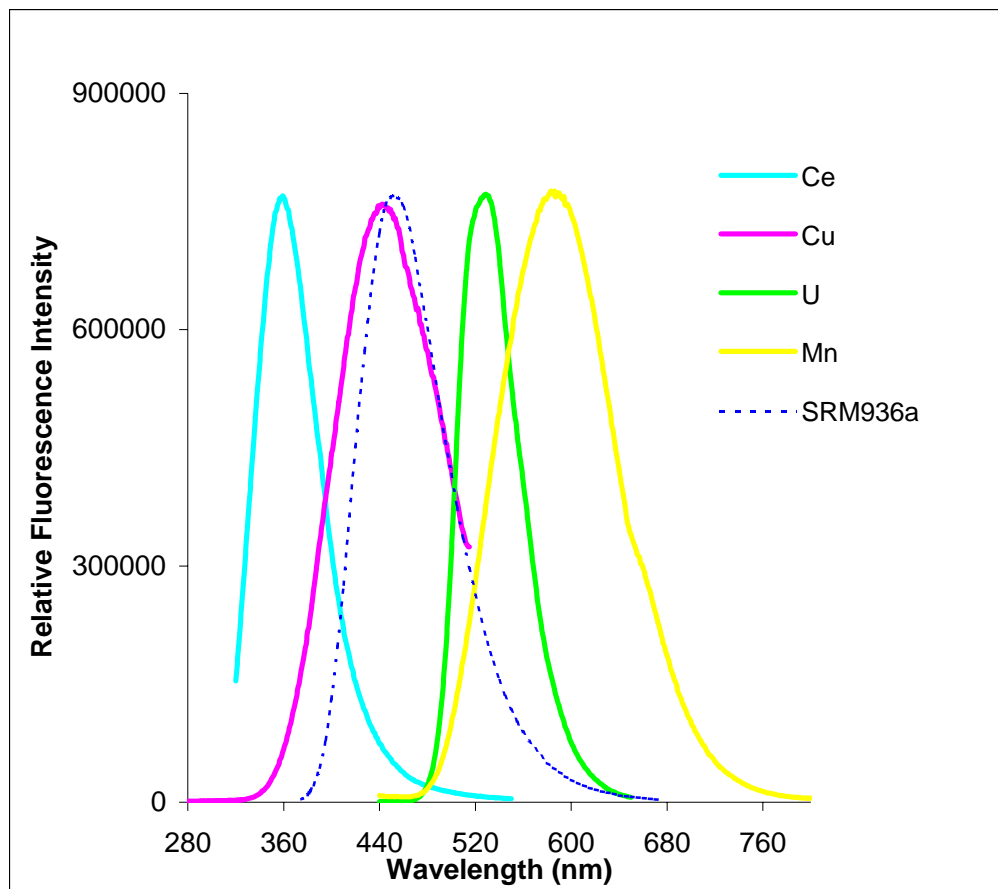
Figure: Spectral emission profiles of each of the four glasses in the suite of standards, compared with that of SRM 936a

Program: Industrial and Analytical Instruments and Services

Title: AnIML—Analytical Information Markup Language

Authors: B.A. Schaefer, D. Poetz, A.D. Nguyen, and G.W. Kramer

Abstract: In collaboration with ASTM Subcommittee E13.15 on Analytical Data, we are creating an extensible markup language (XML) for analytical chemistry result data. Based in part on our previous SpectroML markup language for UV/vis result data, this ASTM effort is being called the Analytical Information Markup Language (AnIML). It is specifically designed for spectroscopy and chromatography data, but its design is generic and modular, making it suitable for use with many different analytical measurement techniques--including those not yet invented.

Purpose: The interchange and storage of analytical chemistry data has long been hampered by multiple, incompatible data formats. Over the past 15 years, several different interchange formats have been developed that allow data generated by different vendor systems of a given technique to be exchanged. For example, using JCAMP-DX, users of most commercial FT-infrared and NMR systems can interchange their respective data. However, in the last few years, the emergence of platform and application independence through the Internet has advanced the possibilities for data interchange beyond the capabilities of these protocols. Today's analytical chemists need not only to interchange data generated within a specific technique, they need to interchange, import, export, store, and combine all their data from multiple sources at multiple sites. Users are now no longer content with just having "pictures" of their data (i.e., data plots). They need real access to their data from within a report itself—they want to be able to expand plots, re-integrate peaks, overlay spectra, etc. without having to revert to the instrument or computer system that generated the original data. And, they don't want to have to purchase, learn, or even load proprietary programs to do this. In industrial settings, experimental data belong to and must be accessible to the entire organization, not just the laboratory personnel that generate it. Proprietary data formats and existing interchange programs simply cannot fill such corporate needs for data accessibility

Major Accomplishments: Over the past three years, we developed an XML-based mechanism for instrument-to-instrument, instrument-to-application, and application-to-application data interchange called SpectroML: an extensible markup language for molecular spectroscopy data. SpectroML was created initially to serve as a model implementation of a markup language for molecular spectroscopy and ultimately to provide a web-based mechanism for interchanging UV/visible spectral data generated on different spectrophotometers with our optical filters database. When our optical filters database was created as a replacement for paper records, we could import data only from the High Accuracy Spectrometer (HAS) used to certify the SRM optical filters. The complex and archaic data importation process badly needed to be modernized, and we wanted to be able to import data from our other spectrometers as well. Using SpectroML drivers/translators for the HAS-II, the PerkinElmer Lambda 900, and the Hewlett-Packard HP 8453 spectrometers, data from these instruments can now be converted into a single format SpectroML file and imported into our optical filters database. SpectroML is an integral part of the process for certifying and recertifying optical filter SRMs; plus, we can import research data taken on machines other than the HAS for comparison purposes.

Even before we developed SpectroML, we began to proselytize both instrument vendors and the ASTM E13 Molecular Spectrometry and Chromatography Committee about the merits of an XML-based approach to data interchange. In 2001, the ASTM E13 committee established a task group to develop a markup language for molecular spectrometry and chromatography, and in 2003 the task group was made into a full ASTM subcommittee—E13.15 on Analytical Data.

E13.15 has been working with instrument vendors and the IUPAC Committee responsible for JCAMP-DX to develop a unified XML-based approach for interchanging molecular spectrometry and chromatography data called the Analytical Information Markup Language (AnIML). AnIML is based on a hierarchical model that calls for the initial development of a core markup language containing the elements common to all applicable analytical techniques. The core schema defining the common notions of sample information, measurement data, system information, quality assurance, etc. will be handled by ASTM E13.15. Technique-specific base documents will build on the core and will be the responsibilities of the respective E13 subcommittees in conjunction with other interested expert groups such as those from the IUPAC, American Society for Mass Spectrometry, etc. Data/instrument vendors are responsible for implementations of the instrument/origin specific base document extensions that will build on both the core and the technique specific standards. Higher-level specifications could include organization-specified extensions that are company-specific and even end-user or application-specific extensions. The core is being built as much as possible to bridge previous data exchange standards work (e.g., ANDI and JCAMP-DX), and efforts are being made to collaborate with and include other organizations with similar interests and as much as possible to reuse terminology and concepts from existing standards.

Over the past year, the schemas for the core and technique definitions have been written and base documents for several techniques have been created. Since the metadata for individual techniques will be maintained in instance documents instead of schemas (to permit extension of technique metadata) the standard mechanism that applications use to validate XML documents syntactically cannot be used. Accordingly, we created a Technique Validator program that provides semantic and syntactical checking as well as some bounds/limits checking for AnIML files. We are now working with several groups of domain experts to develop AnIML. To solve the problem that most of the domain experts do not know XML, we have written a Technique Creator program that guides a user through the creation of a technique base document and then creates the XML code.

Impact: The development of AnIML as a universal molecular spectrometry and chromatography mark up language will revolutionize data interchange, eliminate long standing barriers to data exchange, enable new data manipulation software, facilitate new web-based notions for data usage, and permit the development of realistic schemes for long-term data archival. When coupled with parallel efforts in developing XML approaches to the manipulation of other chemical data, it will pave the way for the fully electronic chemistry data archive, where any known chemical fact or information is but a simple query away on your wireless Personal Digital Assistant from anywhere in the world.

Future Plans: Currently, work is underway in our Group to implement the AnIML core schema and to develop an example implementation of a technique-specific AnIML schema for liquid chromatography photodiode array spectra. If these projects are successful, we can begin implementing AnIML for other techniques. The IUPAC committee has already converted their JCAMP-DX terminology to XML so progress should be rapid for those techniques supported by JCAMP-DX. The AnIML project also dovetails nicely with another IUPAC project to convert the IUPAC units and terminology documents (Green and Gold books) to XML.

Program: Industrial and Analytical Instruments and Services

Title: Molecular Simulation of Alkylsilane Stationary Phases in Liquid Chromatography

Authors: K. Lippa and L.C. Sander

Abstract: Covalently modified surfaces represent a unique state of matter that is not well described by liquid or solid phase models. The chemical bond in tethered alkanes imparts order to the surface in the form of anisotropic properties that are evident in chromatographic and spectroscopic studies. An understanding of the structure, conformation, and organization of alkyl modified surfaces is requisite to the design of improved materials and the optimal utilization of existing materials. Computational simulations offer insights into the structure of covalently modified surfaces that may not be apparent through empirical observation.

Purpose: Simulations offer several advantages over physical experimentation. Models provide a means to visualize the important features of a surface at the molecular level in a way that is not possible by physical experimentation. Models can be precisely described in terms of bonding densities, chain placements, temperature, etc. The influence of changes in specific aspects of the model can be tested directly without altering other parameters. For example, alkyl chain length effects can be studied by extension of existing chains without changing their placement on the silica surface. Simulations can provide insights into the conformation and dynamic aspects of physical materials; however, the utility of the data depends on the suitability and accuracy of the computational approach employed.

Molecular dynamics (MD) is a time-dependent simulation of molecular motion.   Initially, velocities are assigned to atoms (often based on Boltzmann distribution) such that the net momentum is zero (i.e., no flow). After a finite time interval, the energy of the system is calculated. Forces on atoms are calculated, new velocities are determined, and the process is repeated. Coordinates are saved periodically, and analysis of the coordinates over time provide information on molecular motion. Monte Carlo approaches utilize random sampling to choose positions, orientations, etc. of molecules. The energy of each sample is calculated, and the new configuration is accepted or rejected.

Molecular mechanics calculations are typically used to calculate the energy at intermediate steps. Molecular mechanics computations are based on algebraic relations that describe the energy of the molecule(s) in terms of stretching, bending, torsions, electrostatic and van der Waals forces, etc. These terms constitute the force field; any required constants are provided by experiment or ab initio calculation (parameterization).

Major Accomplishments: MD simulation of C_8, C_{18}, and C_{30} modified silicas have been carried out to study changes in stationary phase architecture that may result from variations in chain length, bonding density, synthetic approach, and temperature. Surfaces were modeled using a quartz substrate with vicinal –OH groups (9.8 µmol/m^2), and alkyldimethylsiloxane or alkyldisilanolsiloxane groups were linked via siloxane bonds. Surface densities ranged from 1.6 µmol/m^2 to 5.9 µmol/m^2 for C_8, C_{18}, and C_{30} ligands, and some models were constructed of 3 oligomer units to approximate bonding in polymeric phases. Simulations were carried out with

the COMPASS force field, over time periods long enough so that the structural features were constant (> 800 ps). Several trends were apparent. The thickness of the phases increased with increased bonding density as individual chains were more constrained by neighbors. Correspondingly, the *gauche* fraction also decreased with increased density. At the same bonding density, longer chain length phases were more ordered than shorter chain length phases. Finally, increased order was observed at reduced temperature. The snapshots shown in Figure 1 are representative of low energy conformational states for low density monomeric and high density polymeric C_{18} stationary phases. A high degree of disorder is apparent with models representative of (commercial) monomeric C_{18} columns. Chain extension and increased *trans* conformations are observed with models of polymeric C_{18} phases. C_{30} stationary phase models exhibit significantly increased *trans* conformations, even with lower surface densities (see Figure 2). With the exception of the end methyl group, the distal carbons are primarily *trans*, whereas the proximal carbons have more *gauche* states. It is believed that the *gauche* state is favored in proximal carbons to permit formation and association of *trans* segments at the distal end.

Impact: The models that have resulted from this study clearly indicate the extent of molecular order within alkyl modified surfaces and are consistent with spectroscopic studies (e.g., Raman, ^{13}C NMR, and infrared spectroscopy). The results provide a compelling vision of alkyl modified surfaces that will guide future development of materials for chromatography and biotechnology.

Future Plans: An extension of the simulation effort is planned to probe the effect that various solvent environments in contact with the alkyl modified surface may have on alkyl chain conformation.

Program: Industrial and Analytical Instruments and Services

Title: Determination of Low Level Nitrogen by Radiochemical Neutron Activation
                Analysis
Exploratory Research Project

Authors: R.L. Paul and R.M. Lindstrom

Abstract: A radiochemical neutron activation procedure is being sought to measure low-level nitrogen in steels and other materials. ^{14}C, produced via the ^{14}N(n, p)^{14}C reaction is separated from the sample matrix and quantified by liquid scintillation counting.

Purpose: Many alterations of metal and semiconductors properties are ascribed to the presence of low-level nitrogen. Current industrial methods for measurement of nitrogen are not reliable below 1 mg/kg. Radiochemical neutron activation analysis is capable of detection of nanogram levels of nitrogen in materials. Nitrogen is measured via the ^{14}N(n, p)^{14}C reaction with thermal reactor neutrons. The ^{14}C formed is separated and quantified by beta counting. The method is matrix independent and chemically specific, and since detection is based on a nuclear rather than a chemical reaction, the results are independent of the chemical form of nitrogen. Furthermore, since only radioactive ^{14}C is being quantified, the blank problems inherent in non-nuclear methods for nitrogen analysis are avoided.   The purpose of this work is to develop a reliable RNAA method for measuring nitrogen in metals and other materials, beginning with low alloy steels.

Major Accomplishments: A preliminary procedure was selected, which consisted of oxidation of the steel by fusion with Pb_3O_4/B_2O_3 in an enclosed system under a flow of argon. Evolved $^{14}CO_2$ is absorbed in a liquid scintillation cocktail and ^{14}C measured by liquid scintillation counting. The procedure was tested using a measured quantity of a ^{14}C tracer solution with 1 g of steel. Repeated trials failed to yield consistent ^{14}C count rates or complete recovery of ^{14}C activity. This procedure suffers from several problems. The Pb_3O_4/B_2O_3 fusion is lengthy and expensive (a new alumina crucible is required for every sample and the quartz combustion tube is complex). Even after an hour at 950° some unreacted steel remained in the melt; the method is also known not to attack graphite. In addition, there is no way to determine the fraction of ^{14}C recovered from the sample.

Several alternative procedures for oxidation of the sample have been tried. The most promising method of attack is simple combustion in flowing oxygen at 900° to 1000°, with or without an accelerator, a method that has been used in the analysis of carbon in steel for many years.

The problem of determination of ^{14}C recovery fraction may be solved by following the procedure outlined in Figure 1. The sample is mixed with a known amount of nonradioactive carrier ($CaCO_3$), before oxidation. The evolved CO_2 is precipitated as $BaCO_3$, which is then weighed to determine the chemical yield and decomposed with HCl. Evolved CO_2 is quantitatively absorbed in the scintillator cocktail. Tests have verified that the fraction of $BaCO_3$ recovered is near 100 %.   A known quantity of a ^{14}C labeled $BaCO_3$ was decomposed with HCl, and $^{14}CO_2$ absorbed in scintillation cocktail. Repeated trials yielded consistent and quantitative results.

Potential Impact: A reliable method for measurement of nitrogen in a wide variety of materials could impact many industries. Foremost on this list is the U. S. aerospace industry, which requires primary standards for accurate measurement of low-level nitrogen in titanium. The RNAA method could be provide the industry with the means to improve safety standards for aircraft. The method could be extended to analysis of other materials, especially biologicals, where determination of nitrogen in proteins is essential.

Future Plans: Preliminary measurements indicate that the proposed scheme has a high probability of success. This scheme will be tested first by burning samples of un-irradiated steel mixed with $CaCO_3$ carrier and a known amount of ^{14}C tracer. If the ^{14}C can be quantitatively measured, then the method will be further tested through analysis of several NIST SRM steels that are certified for nitrogen.

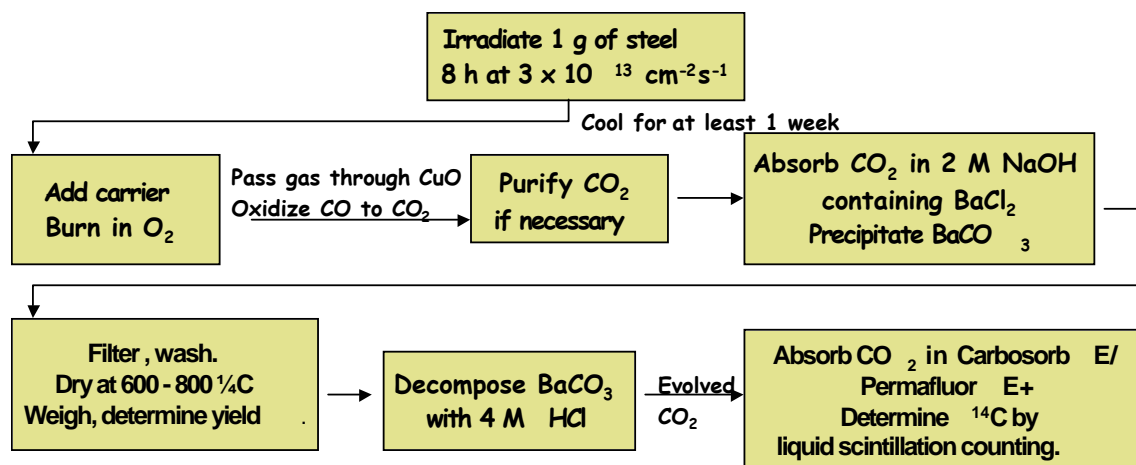Figure 1. Procedure for determination of N in steels by RNAA

Monomeric C$_{18}$
(2.5 μmol/m^2)

Polymeric C$_{18}$
(4.9 μmol/m^2)

Figure 2. Top and side view snapshots from simulations of monomeric and polymeric C$_{18}$ stationary phases.

A) Monomeric C$_{18}$
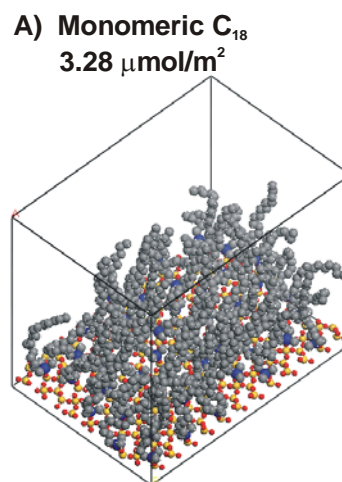**3.28 μmol/m^2**
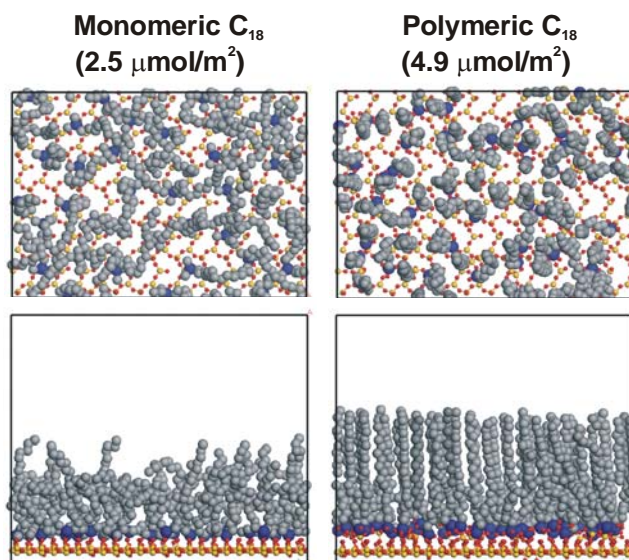
Figure 3. Snapshots of simulations of (A) monomeric C$_{18}$ and (B) monomeric C$_{30}$ modified surfaces.

B) Monomeric C$_{30}$
2.73 μmol/m^2
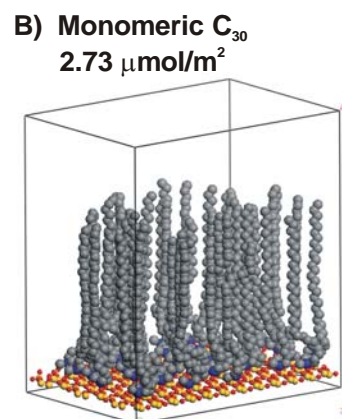
Program: Industrial and Analytical Instruments and Services

Title: Investigation of Arsenic Oxidation State Speciation in Primary Calibration Solutions and Effects on ICP-OES Measurements

Authors: L.L. Yu, T.A. Butler, and G.C. Turk

Abstract: It is well known that the toxicity of arsenic is strongly tied to oxidation state speciation. Less understood is the effect that arsenic oxidation state has on measurement accuracy.   Standards prepared from arsenic metal, which in principle should yield a more accurate and precise standard relative to those prepared from an arsenic compound, were frequently found to have inexplicable disagreements between batches when analyzed by using optical emission or mass spectrometry. The deviation, which can at times be as great as a few percent, frustrates the efforts of producing an accurate clinical standard for arsenic. Our studies of the cause of this disagreement between the arsenic standards point to differences in arsenic valence states between solutions. The results of an investigation into the kinetics of the reaction for the arsenic standard preparation elucidated why arsenic solutions comprised of varied arsenic species were produced. Guidelines were developed based on the investigation for producing a single species arsenic standard, thus eliminating the measurement bias in the certification process, ensuring the production of more accurate and precise arsenic standards for clinical and general use.

Purpose: To produce a highly precise and accurate arsenic standard by investigating and eliminating an unexplained bias between gravimetric preparation value and the inductively coupled plasma optical emission spectrometric value of arsenic standards.

Major Accomplishments: We analyzed sets of standard solutions prepared by dissolving arsenic metal with nitric acid and found both arsenic III and arsenic V to be present in these standards, including various lots of SRM 3103a, the arsenic spectrometric solution. Furthermore, we discovered that standards containing greater amounts of As III yielded somewhat lower signals in ICP Optical Emission Spectrometry than those in which the predominant form of arsenic was As V. Similar results have also been observed using ICP Mass Spectrometry. This difference in the instrumental response of these two forms of arsenic will result in a measurement bias if samples and calibration standards differ in the form of arsenic. The figure below shows the results of a study of the kinetics of the arsenic metal digestion process. In the experiment small aliquots of solution were periodically withdrawn over a period of 40 hours from a digestion vessel as a piece of arsenic metal was being dissolved in a 50 % (v/v) solution of concentrated nitric acid in water on a warm hotplate. The withdrawn aliquots were analyzed using liquid chromatography with ICPMS detection to determine the fraction of the total dissolved arsenic present as As III. The results show that at the beginning of the process most of the solution is present as As III, and all of the solution is present as As V after 25 hours. This discontinuities in the reaction curve occur when additional nitric acid / water is added. All of the metal appears to be dissolved after only 15 hours. If the process had been stopped after 15 hours, the resulting solution would contain a mixture of arsenic oxidation states. It is clear that this situation occasionally occurs in our production of arsenic solution standards, including SRM 3103a. We have now developed a procedure utilizing iodine as an oxidant to convert solution

standards containing mixed oxidation states of arsenic to As V, thus eliminating the source of bias.

Kinetic Study of As Metal Digestion
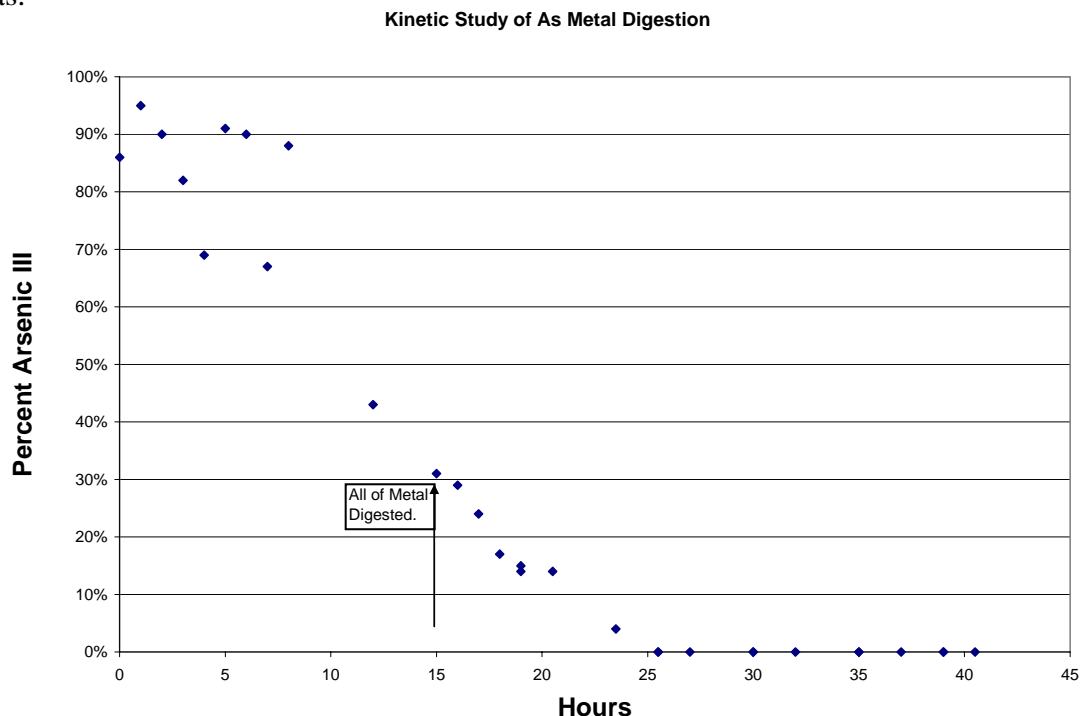
Impact: The result of the research resolves a long-standing mystery regarding bias sometimes observed between the gravimetric preparation value of certain arsenic solutions and values determined spectrometrically using independent calibration solutions. A revised digestion procedure developed as a result of this research ensure the production of a more accurate and precise arsenic standard for clinical and general applications. The research also raises some questions regarding the accuracy of arsenic measurements by using plasma source based spectrometry techniques.

Future Plans: Further studies will determine if other elements are susceptible to similar systematic bias. The underlying cause of the bias in plasma source spectrometry remains unknown.